BIMONTHLY REPORT NO. 1

ON THE

WATER-ACTIVATED BATTERY

Period: 22 June 1959 – 21 August 1959   25X1

Prepared by: 25X1

25X1

DOC	10	REV DATE	2 APR 1980	BY	064540
ORIG COMP	056	OPI	56	TYPE	30
ORIG CLASS	M	PAGES	70	REV CLASS	C
JUST	22	NEXT REV	2010	AUTH:	HR 10-2

ORIGINAL CL BY 235979
☐ DECL ☒   02/04/2010
EXT BY   SAME
REASON 3 d (3)

CONFIDENTIAL

TABLE OF CONTENTS

CONFIDENTIAL

I. ABSTRACT

It is the purpose of this study to demonstrate the feasibility of a compact (10.4" x 3.5" x 1.6"), chemically rechargeable, water acti-vated battery, delivering an average current of 3 A at 12 V for at least 60 minutes under normal operating conditions. Its performance under adverse operating conditions is also to be studied.

Since the procurement of silver clad magnesium foil, an impor-tant ingredient of the chemical charge, proved to be impossible, it was necessary to develop a new technique for producing a suitable bond between silver and magnesium foils. This has been our major activity during the reporting period. The suitability of our new screen press method for producing such bonds has been ascertained by small scale battery tests.

Basic calculations predict an internal generation of heat equivalent to about 180 Watts for a standard electrical output of 36 Watts.

II. PURPOSE

Phase 1:

To demonstrate the feasibility of a large model, chemically rechargeable, magnesium-silver chloride battery, activated by a 3 per cent salt solution at room temperature and delivering an average current of 3 A at 12 V for at least 60 minutes. The voltage regulation at a maximum load current of 5.3 A shall equal or surpass the stability

-1-

obtained previously.

Phase 2:

To demonstrate **reasonably satisfactory performance** of this battery at environmental temperatures of $-40^{\circ}C$ and $40^{\circ}C$, using a variety of electrolytes such as 3 per cent salt solution, tap water and others. It is recognized, however, that such performance cannot be expected to match that at room temperature.

Phase 3:

To fabricate and deliver **six battery cases** and thirty complete sets of chemical recharges for field testing purposes, including instructions on the proper handling, **activation**, deactivation, disposal and temperature control.

III.   FUNDAMENTALS

The performance behavior of the battery, to be developed, can best be understood in terms of its basic reactions and discharge mechanisms.* The most important features can be represented by the following two reactions:

a) $Mg + 2AgCl \longrightarrow MgCl_2 + 2Ag + W + H_a$ (40%)

b) $Mg + 2H_2O \longrightarrow Mg(OH)_2\downarrow + H_2\uparrow + H_b$ (60%)

---
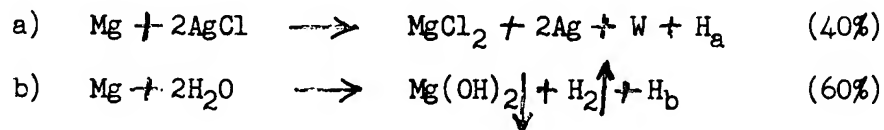
* Only part of this information has been included in the <u>Annual Report on the Energy Sources Study</u>, July 1, 1957 to June 30, 1958: $\boxed{}$ 25X1

$\boxed{}$, pp 49 and 54. This will be referred to as the "Annual Report".   25X1

-2-

Under normal load conditions only about 40 per cent of the reacting magnesium contributes to the production of electrical output W, according to a). The rest is oxidized at the anode without producing any electricity, as indicated by b).

Both reactions a) and b) contribute to the generation of heat. For a) the evolution of heat can be estimated from the degree of irreversibility of the electrochemical reaction. Since the theoretical cell EMF is about 2.5 V, whereas the actual cell voltage under load is only 1.33 V, the heat equivalent H_a of this voltage differential (1.17 V) can be calculated. Such data have been tabulated in Table I. At an assumed overall discharge rate of 1 Mol of magnesium per hour $W = 14.3$ Watts and $H_a = 12.6$ Watt equivalents. The heat of formation of reaction b) can be calculated at 84 K cal/mol, which yields a heat evolution H_b of 59 Watt equivalents. As indicated in Table I the total heat generated H is equivalent to nearly five times the electrical output. Since the required average output of the battery to be built is 3 A at 12 V (36 Watts), the expected rate of heat generation can be assumed to be about 180 W for the rated load condition. For other loads the values of H will be proportionately higher or lower. In case of a short-circuit, H can be 15 x or even 20 x the rated value. Naturally, such a heating effect (2.7 - 3.6 KW) will produce a rapid rise of the battery temperature. We are planning to take advantage of this short-circuit heating effect for the activation of the battery at low temperatures (Phase 2).

TABLE I

Discharge Features

(Rate: 1 Mol of Mg per hour)

Reaction		Electrical Output W Watts	Heat · Generated H Watt Eq.	Discharge Products
Type	Rate Mol/hr			
a)	0.4	14.3	12.6	Low resistivity Electrolyte and Filamentary Silver
b)	0.6	0	59	Hydrogen Gas and Precipitate
TOTAL	1.0	14.3	71.6	$\dfrac{H_a + H_b}{W} \approx 5$

IV. PAST ACHIEVEMENTS

The decision to initiate a feasibility study on a water-activated magnesium-silver chloride system, made in September 1957, was based on the following promising features:

1) The electrolyte is universally available.

2) The chemical recharging process involves only the handling of mechanically stable, chemically harmless foils which can easily be packaged and inserted into the battery case.

3) Current densities (250 mA per inch^2) are high enough for the operation of portable transmitters with adequate voltage regulation.

4) Enough heat is generated internally to facilitate satisfactory performance in low temperature environments. (See previous section).

5) The disposal of discharged materials is easy and safe.

Details on the small scale realization of some of these features can be found in the Annual Report.[*] We shall summarize here the performances of only one, for easy reference. Run No. 33 (page 61, Fig. 30), illustrates the load characteristics and chemical rechargeability of a 9-cell battery, with cell areas of 1.875 square inches (3/4"ʒ 2 1'2"). This battery was subjected to an intermittent discharge, delivering

---

[*] Abstract, Summary and Sections IV-D and V-B, (pp 2, 3, 34, 35, 47-63, 81, 82).

0.283 Ampere-hours during a 60 minute period (average current 0.283 A) with peak loads of 0.5 A and with load voltages in excess of 12 V at all times. During this run, voltage fluctuations varied from a maximum value of 14 per cent at the beginning of the run down to 6 per cent at the end. A 3 per cent sodium chloride solution was used as the electrolyte and, although this test was performed at room temperature, the average battery temperature increased to $55^{\circ}C$. The design of the larger battery, to be described in the next section, is largely based on the performance of this run.

During the previous contract period it was not possible to produce or procure a satisfactory bond between the magnesium and silver foils, thereby preventing the excess corrosion of magnesium, described on page 57-60 of the Annual Report. Nevertheless, the scope of the present contract is based on the commercial availability of silver clad magnesium and the procurement of such material is to be initiated at the earliest possible time.

V. FACTUAL DATA

    A. Development of a Technique for the Bonding of Thin Silver to Magnesium Foils

        1. Introduction

Prior to the starting date of this contract, inquiries leading towards the procurement of a sizable quantity of silver clad magnesium foil were made. Unfortunately, companies such as Metals and Controls

-6-

Corp., General Plate Division, Attleboro, Massachusetts, who had pre-
viously supplied us with excellent small samples of such material, could
not be persuaded to submit any quotes. Apparently the cleanliness re-
quirements for the satisfactory direct bonding of silver to magnesium
are too stringent. As a result of this setback, it became necessary for
us to develop our own new method for the bonding of a thin silver foil to
magnesium. Practically all our efforts during this reporting period have
been devoted to this development. The requirements are as follows:

a)   Adequate mechanical adhesion at all

operating temperatures (-40°C to 100°C).

b)   Adequate sealing to prevent the back side

corrosion of the magnesium foil.

c)   Low electrical contact resistivity for

minimum internal resistance of the battery.

d)   Excellent chemical stability.

e)   Ease of fabrication.

2.   Exploratory Tests

The adhesive and sealing properties of our experimen-
tal packages (requirements a) and b)) can be determined easily by peeling
off the silver foil either before or after treatment in hot salt solutions.
The measurement of contact resistances, on the other hand, requires the
development of a special test circuit, illustrated in Figure 1. In it
the small voltage drop across the silver-magnesium boundary layer, caused
by a DC current I (0.5 - 3.5 Amp.), can be measured by means of a sensitive

-7-
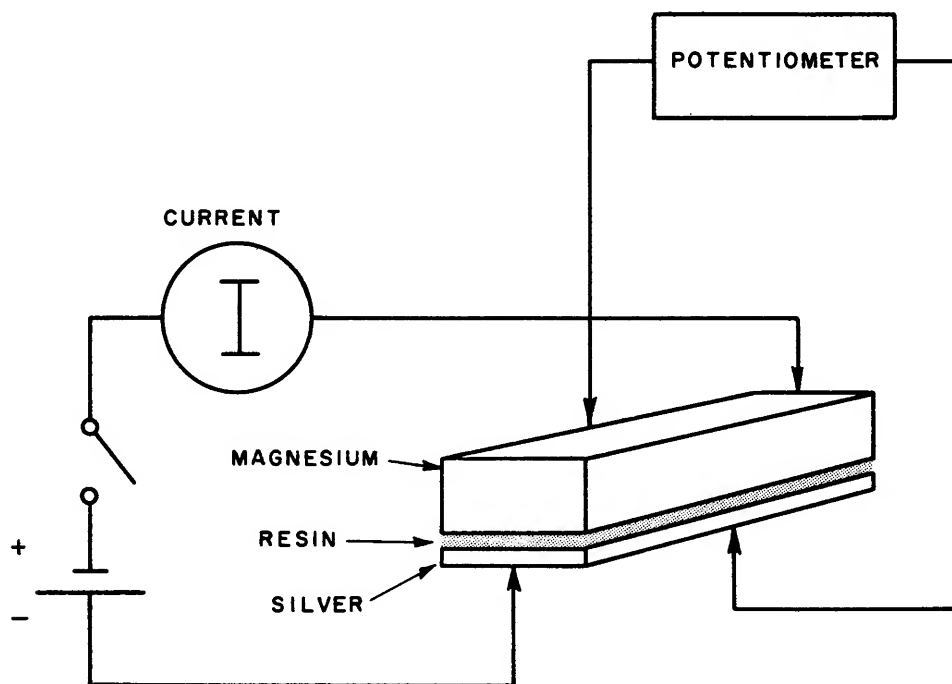
CIRCUIT FOR THE MEASUREMENT OF CONTACT RESISTANCES

FIGURE I

potentiometer. IR-drops in the foils themselves may complicate the interpretation of such measurements, unless special care is taken. The symmetrical arrangement of the electrodes, shown in Figure 1, tends to minimize these effects of foil resistance. The minimum detectable contact resistance of this simple arrangement is about 30 Microhms per square inch, far below the requirements for this application.

Contact resistance measurements have also been used to detect gradual changes of bond resistances prior to activation. However, there is no real substitute for actual battery tests, to determine the suitability of any new bonding technique and such tests have been used repeatedly. In the interest of speed and materials economy the existing improved groove battery, described on page 61 of the Annual Report, has been used for such purposes.

Our first exploratory bonding tests involved the use of a thin layer of high temperature epoxy resin*. Such layers were sprayed onto the magnesium and/or silver foils. After evaporation of the thinner this resin can be cured at a high temperature as follows:

Temperature	Duration
150°C	20 minutes
100°C	90 minutes

The application of hydraulic pressure to the magnesium-resin-silver foil package during the cure should provide enough metallic contact points

---

* Hysol 6101B; Houghton Laboratories, Olean, New York.

-9-

between the magnesium and silver to yield a contact resistance less than
0.1 Ohm per square inch. For a battery current density of 250 mA per
square inch, this value may be considered to represent a very conserva-
tive upper limit. As expected, it was found that after curing for 1/2
hour at $150^{\circ}C$ and 800 lbs/$inch^2$ pressure, very low contact resistances
of the order of 10^{-2} - 10^{-3} Ohm per $inch^2$ were obtained, and it was
believed that the other requirements, listed previously, were well
satisfied. Unfortunately, battery load tests, using this type of bond,
were inferior to those obtained previously. The low contact resistances,
measured separately in our test circuit, could not be maintained during
a run. Attempts to improve the stability of this bond by spot welding
failed. The presence of this type of resin layer seriously impairs the
passage of localized high current pulses.

Next we investigated the suitability of conductive coatings as
a bonding material. Hysol 6251, a silver powder loaded epoxy resin, was
used primarily. Its full curing schedules are as follows:

| Temperature	Duration
$20^{\circ}C$	24 hours
$60^{\circ}C$	90 minutes
$150^{\circ}C$	7 minutes
$204^{\circ}C$	2 minutes

Except for details the same bonding procedure was followed and the re-
sultant contact resistances were found to be substantially lower. The
adherence of this material to the magnesium foil was found to be very

-10-

poor. However, after first sputtering the magnesium foils with silver or depositing electrolytically a thin layer of copper on one side, adherence was greatly improved. In spite of all these added features the battery performance remains below standard, particularly at higher temperatures. Consequently, this approach was also abandoned.

3. The Screen Press Method

Of all the exploratory tests, the most significant ones of which have been summarized in the previous section, those using the high temperature resin, Hysol 6101B, would show considerable promise if it were possible to improve and stabilize their contact resistance. This has been made possible by "localizing" the pressure during the curing operation, thereby creating a large number (10^4 per inch^2) of well defined local contact points, as indicated by the arrows in Figure 2. Each of these contact points is surrounded by a resin layer for good adherence and sealing. The contact resistance of such a layer is below the limit measurable with our instrument. Nevertheless, its performance is further improved and stabilized by conventional spot welding, following the cure. The resin layer no longer interferes with this operation.

While localized pressure can be realized by means of a variety of methods, only the preferred screen press technique shall be described here. It has been found that the inhomogeneous pressure distribution, resulting from the insertion of a standard sieve adjacent to the silver foil during the pressing operation, produces the desired localized pressure at the magnesium-silver interface.

-11-
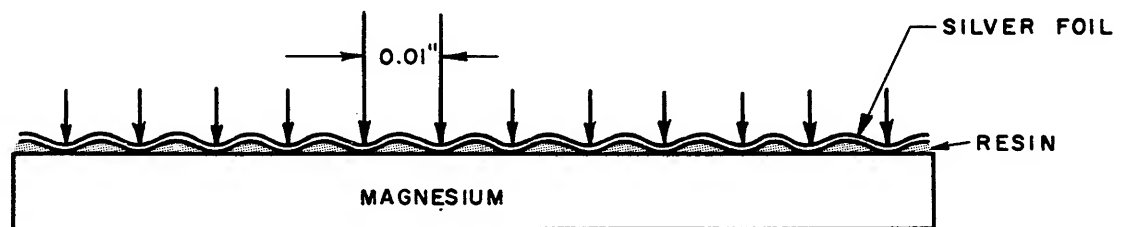
CROSS SECTIONAL VIEW OF A SCREEN PRESS BOND

FIGURE 2

-12-

Rectangular pieces of magnesium alloy (DOW J1) 9.4" x 3" x 0.012",
after cleaning with steel wool and acetone, are sprayed on one side with
Hysol 6101B, properly thinned with solvent #1514 to yield a resin layer
less than 0.0005" thick. Drying of the resin layer is accelerated by
placing the sheets for 10 minutes in a $100^{o}C$ oven. Subsequently, the
drying is continued to completion at room temperature for at least 8 hours.
The slightly larger annealed silver foils, thickness 0.001", are cleaned
similarly. No resin is applied to them.

The following package is positioned on top of the press base:

a) Bottom steel plate 5/8" thick, ground flat.

b) 1/16" thick high temperature silicone rubber sheet
    fitted into a 1/16" thick brass frame.

c) Magnesium sheet with resin layer facing item d).

d) Silver foil.

e) Aluminum foil, 0.001" thick.

f) 100 Mesh Screen.

g) Top steel plate, identical to item a).

Item b), together with items a) and g), equalizes the hydraulic
pressure over the entire surface area. Its closely fitting surrounding
brass frame prevents it from expanding sideways. Item e) prevents any
excess resin, squeezed out around the edges of item c) during the pressure
cycle, from clogging the screen, item f).

The press heaters are turned on, while a pressure of about 700
$lbs/inch^2$ is maintained. After 20-30 minutes the desired maximum temperature

-13-

CONFIDENTIAL

of 150°C has been reached. It is held at that level for 20 minutes, where-upon the temperature is rapidly lowered by means of water cooling.

The pressure is released only after the temperature has dropped below 50°C. The magnesium-silver bond is now ready for spot welding. These spots are placed about 1/4" apart. Battery discharge tests, using components prepared according to this screen press method, indicate superior performance.

B. Battery Design

Concurrent with the new component development just described, the design of the large model battery, featuring cell surface areas of 24 inch^2, has been completed. The overall dimensions of the battery case are to be 3.5"(H) 1.6"(W) 10.4"(L). All materials required for the entire program are on order and two battery cases are being built. Since no test results are available at this time, a detailed discussion of the large model battery design will be deferred until the next report.

VI. CONCLUSIONS

A substitute package for replacing silver clad magnesium, a primary material for this battery project, has been developed. The bonding of silver to magnesium foils has been achieved by means of the screen press method and its satisfactory performance has been ascer-tained by small scale tests. While it has taken two months of intensive work to develop this technique, we are now ready to proceed with the development of the large scale battery model.
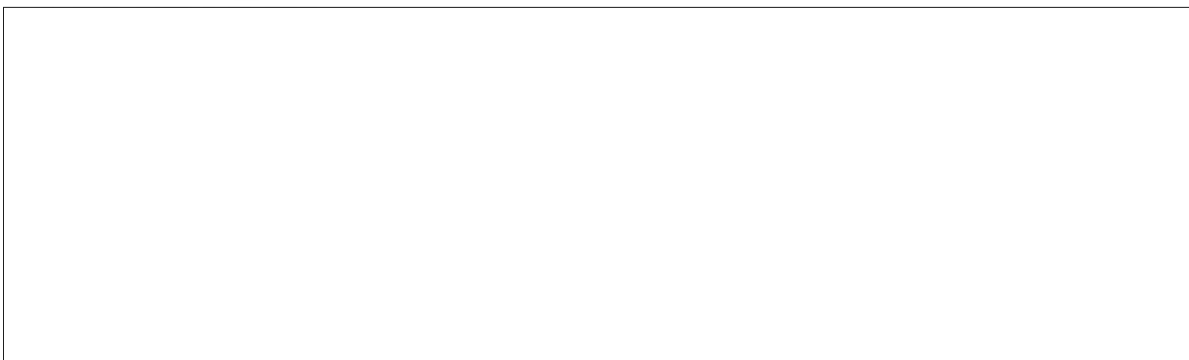
-14-

CONFIDENTIAL

CONFIDENTIAL

Basic calculations predict a surprisingly large amount of heat generation, accompanying the generation of electricity. This heat is expected to be the equivalent of about 180 Watts for standard output, or 5 times the electrical power drawn. This will affect substantially the thermal behavior of the battery.

VII. FUTURE PLANS

With the construction of the large battery cases progressing satisfactorily and with an adequate supply of materials at hand, the completion of Phase I towards the end of the next reporting period can be expected.

VIII. PERSONNEL

25X1

-15-

CONFIDENTIAL